Structural Diversity in Lanthanide Phosphido Complexes. Formation and X-ray Crystal Structure Determination of an Unusual Dinuclear Phosphido Complex of Divalent Samarium: [(Me₃Si)₂P]Sm[μ-P(SiMe₃)₂]₃Sm(thf)₃·C₇H₈[1]

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*Summary: The dinuclear phosphido complex of divalent samarium [(Me₃Si)₂P]Sm[μ-P(SiMe₃)₂]₃Sm(thf)₃ (**1**) can be readily made from SmI₂(thf)₂ and 2 equiv of KP-(SiMe₃)₂ in tetrahydrofuran solution. The unusual molecular structure of complex **1** in the solid state is discussed.*

Amido species of both divalent[2] and trivalent[3−6] lanthanide elements have been intensively studied during the past two decades. We were interested in a comparison of homologous binary amido and phosphido complexes of the lanthanides.

Recently, we reported on the synthesis and structural characterization of two novel trivalent homoleptic lanthanide phosphido complexes of the general formula Ln-[P(SiMe₃)₂]₃(thf)₂ (Ln = Tm, Nd).[7] These results show clearly that the coordination sphere around the lanthanide center is not as sterically saturated as in the case of the corrresponding tris[bis(trimethylsilyl)amido] species, thus allowing for the coordination of two solvent molecules in axial positions. Efforts have been undertaken now to extend this comparative study to divalent lanthanide species.

Evans and co-workers reported earlier on the synthesis and X-ray crystal structure determination of divalent monometallic Sm[N(SiMe₃)₂]₂(thf)₂.[2] Here we describe the preparation and crystal structure determination of [(Me₃Si)₂P]Sm[μ-P(SiMe₃)₂]₃Sm(thf)₃ (**1**) (Figure 1), which is obtained from the reaction of SmI₂-(thf)₂[8] and 2 equiv of KP(SiMe₃)₂[9] in tetrahydrofuran solution at room temperature. A comparison of these two analogous amido and phosphido complexes with respect to their solid state structures shows that in the case of the phosphido species **1** a bimetallic species is
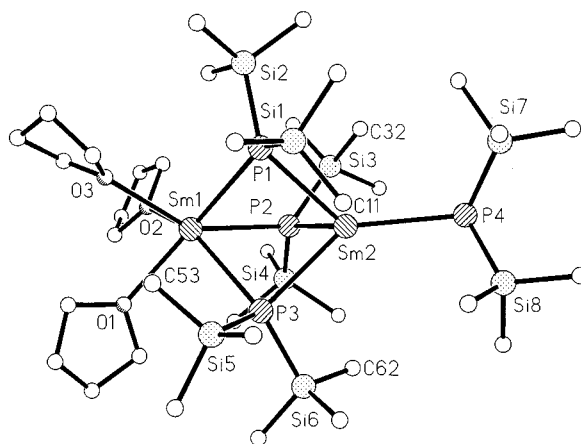
Figure 1. Molecular structure of [(Me₃Si)₂P]Sm[μ-P(SiMe₃)₂]₃Sm(thf)₃ (**1**) (SCHAKAL, H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Sm-(1)−P(1) 3.178 (3), Sm(1)−P(2) 3.165 (3), Sm(1)−P(3) 3.100 (3), Sm(1)−O(1) 2.597 (8), Sm(1)−O(2) 2.571 (7), Sm(1)−O(3) 2.610 (8), Sm(2)−P(1) 3.019 (3), Sm(2)−P(2) 3.033 (3), Sm(2)−P(3) 3.066 (3), Sm(2)−P(4) 3.027 (3); P(2)−Sm(1)−P(1) 81.6 (1), P(3)−Sm(1)−P(1) 79.4 (1), P(3)−Sm(1)−P(2) 81.1 (1), O(1)−Sm(1)−P(1) 151.0 (2), O(1)−Sm(1)−P(2) 121.0 (2), O(1)−Sm(1)−P(3) 86.1 (2), O(2)−Sm(1)−P(1) 126.1 (2), O(2)−Sm(1)−P(2) 84.3 (2), O(2)−Sm(1)−P(3) 148.2 (2), O(2)−Sm(1)−O(1) 77.5 (2), O(3)−Sm(1)−P(1) 87.5 (2), O(3)−Sm(1)−P(2) 145.9 (2), O(3)−Sm(1)−P(3) 128.5 (2), O(3)−Sm(1)−O(1) 82.1 (2), O(3)−Sm(1)−O(2) 76.3 (2), P(2)−Sm(2)−P(1) 86.4 (1), P(3)−Sm(2)−P(1) 82.5 (1), P(3)−Sm(2)−P(2) 83.8 (1), P(4)−Sm(2)−P(1) 129.0 (1), P(4)−Sm-(2)−P(2) 120.8 (1), P(4)−Sm(2)−P(3) 137.6 (1), Sm(2)−P(1)−Sm(1) 80.7 (1), Sm(2)−P(2)−Sm(1) 80.7 (1), Sm(2)−P(3)−Sm(1) 81.2 (1).

being formed versus a monometallic system in the case of the bis(amido) complex. This new disilylphosphido complex has also been examined in solution by variable-temperature ¹H NMR spectroscopy.

Buhro and co-workers reported earlier that P(SiMe₃)₂ complexes are found to exhibit higher molecularities and higher coordination numbers than the homologous N(SiMe₃)₂ complexes.[10] The differing behaviors of these two classes of ligands were ascribed to normal periodic trends that distinguish the properties of N and P, e.g., lower electronegativity, larger size, and lower hybridization tendency of P.

The molecular structure of **1** is unique in lanthanide chemistry and differs significantly from the solid state

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structures reported for divalent lanthanide bis(diphenylphosphido) complexes of the general formula Ln-[PPh$_2$]$_2$(L)$_4$ (Ln = Sm, Yb; L = thf, *N*-methylimidazole).[11] These species were found to be hexacoordinated lanthanide complexes in slightly distorted octahedral environments with the phosphido ligands in *trans* positions. Additionally, the crystal structure of the title compound is clearly different from other structural types we reported earlier in the area of lanthanide phosphido chemistry, namely, trivalent (ᵗBu$_2$P)$_2$La[(μ-PᵗBu$_2$)$_2$Li(thf)] and divalent Yb[(μ-PᵗBu$_2$)$_2$Li(thf)]$_2$.[12]

The molecular structure of **1**[13] features the two samarium centers in different coordination environments. The asymmetry of the title complex is unusual but is somewhat reminiscent of the europium amide [(Me$_3$Si)$_2$N]Eu[μ-N(SiMe$_3$)$_2$]$_2$Na.[14] Sm(1) is surrounded by three thf ligands as well as three bridging phosphido ligands. The arrangement of ligands around Sm(1) can best be described as slightly distorted trigonal prismatic with an average twist angle of 16° between the two triangles. Contrary to Sm(1), Sm(2) is surrounded by four only-phosphorus containing substituents, three bridging and one terminal phosphido ligand. Two of the three bridging Sm(1)−P distances are significantly longer [Sm(1)−P(1) 3.178 (3) Å; Sm(1)−P(2) 3.165 (3) Å] than the third one [Sm(1)−P(3) 3.100 (3) Å]. The opposite observation is made in the case of tetracoordinated Sm(2): the bond distances for Sm(2)−P(1) [3.019 (3) Å] as well as for Sm(2)−P(2) [3.033 (3) Å] are clearly shorter than Sm(2)−P(3) [3.066 (3) Å]. One would expect the terminal Sm(2)−P(4) distance to be shorter than the bridging Sm(2)−P(1) to Sm(2)−P(3) distances. However, the terminal Sm(2)−P(4) bond distance of 3.027 (3) Å was found to match the Sm(2)−P(1) as well as the Sm(2)−P(2) bond distances within the error limits. These Sm−P distances are also significantly shorter than the Sm−P distance of 3.1908 (6) Å reported for hexacoordinated (η^1-C$_{12}$H$_8$)$_2$Sm(thf)$_4$,[15] the Sm−P distance of 3.139 (3) Å in hexacoordinated Sm[PPh$_2$]$_2$(*N*-MeIm)$_4$[11a] (*N*-MeIm = *N*-methylimidazole), and the corresponding distance of 3.0775 (1) Å in (η^5-2,3-(CH$_3$)$_2$(C$_9$H$_6$P)$_2$Sm(thf)$_2$.[15]

Agostic interactions are present in complex **1**, for both Sm(1) and Sm(2). Therefore, an accurate determination of the coordination numbers for both metal centers is difficult. The closest nonbonding Sm···C distances are

3.689 (11) [Sm(1)···C(53)]; 3.257 (11) [Sm(2)···C(11)]; 3.454 (13) Å [Sm(2)···C(32)], and 3.747 (13) Å [Sm(2)···C(62)]. These numbers can be compared with reports from Evans and co-workers on agostic interactions in the two monometallic complexes of divalent samarium, Sm[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ [3.32 (1)−3.46 (1) Å][2] and (C$_5$Me$_5$)$_2$-Sm [3.22 (1) Å].[16]

The nonbonding Sm···Sm distance in complex **1** is 4.014 (2) Å. Sm(1) deviates 2.09 (2) Å from the plane described by the three bridging phosphorus atoms P(1), P(2), and P(3). The corresponding distance for Sm(2) is 1.92 (2) Å. The arrangement of Sm(1), Sm(2), and P(4) is almost linear with a Sm(1)···Sm(2)···P(4) angle of 171.0°.

The P−Si distances in **1** are 2.195 (4)−2.218 (4) Å [average 2.206 (7) Å] with Si−P−Si angles ranging from 102.6 (1) to 104.1 (1)° [average 103.4 (3)°]. The dihedral angles between the PSi$_2$ planes and the P$_3$ plane are 33.2° [P(1)], 25.6° [P(2)], and 30.2° [P(3)]. The sum of angles around P(4) is 326.7°, thus showing a distinctly pyramidal environment around P(4). The geometry around the P(4) ligand in **1** can be compared with the gas phase structure[17] of tris(trimethylsilyl)phosphine [sum of angles around phosphorus 315.6°, average P−Si distances of 2.259 (1) Å, and average Si−P−Si angles of 105.1 (2)°] and the solid state structure[18] of tris(trimethylsilyl)phosphine [sum of angles around phosphorus 318.1°, average P−Si distances of 2.245 (3) Å, and average Si−P−Si angles of 106.0 (3)°], both of which exhibit a distinctly pyramidal environment around phosphorus.

Since complex **1** has a rather peculiar structure in the solid state, we were interested in investigating its solution structure in different solvent media. Due to the strong paramagnetism of samarium(II) as well as fluxional behavior of complex **1** in solution, we were unable to detect any signals in the ^{13}C or ^{31}P NMR spectra at room temperature.

A VT ^{1}H NMR study of **1**·C$_7$H$_8$ in both deuterated toluene and deuterated tetrahydrofuran revealed that the solution structure of complex **1** must be different from the molecular structure observed in the solid state. Details are given in the Experimental Section. However, it needs to be pointed out that the nature of the molecular structure of complex **1** in toluene or tetrahydrofuran solution is not clear.

The synthesis and structural characterization of the title compound provides easy access to a novel phosphido species of divalent samarium. The utility of **1** remains to be determined by its chemistry in a variety of systems.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk double-manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. SmI$_2$(thf)$_2$ was prepared from samarium metal (Strem) and 1,2-diiodoethane (Aldrich).[8] KP-(SiMe$_3$)$_2$ was prepared according to the literature.[9]

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(13) Crystal data for **1**·C$_7$H$_8$ (C$_{43}$H$_{104}$O$_3$P$_4$Si$_8$Sm$_2$): M_r = 1318.59; orthorhombic, space group $P2_12_12_1$ with a = 12.561 (2) Å, b = 22.122 (3) Å, c = 24.595 (3) Å, V = 6834.3 Å^3, ρ = 1.281 g cm^{-3}, Z = 4, $F(000)$ = 2728; Enraf Nonius CAD4 diffractometer. The structure was solved by direct methods. Data collected at 211K with Mo Kα (λ = 0.710 69 Å). Data were corrected for Lorentz and polarization effects as well as for decay (−16.7%) and absorption [empirical, T_{min} = 0.83, T_{max} = 0.99, μ(Mo Kα) = 19.67 cm^{-1}]. From 12 608 measured [(sin Θ/λ)$_{max}$ = 0.59 Å^{-1}] and 11 796 unique reflections, 10 490 were considered "observed" [F_o > 4σ(F_o)] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters except for the C atoms of the solvent toluene, which was treated as a rigid group. All H atoms were calculated and allowed to ride on their corresponding carbon atom with fixed isotropic contributions ($U_{iso(fix)}$ = 0.08 and 0.15 Å^2, respectively). The structure converged for 506 refined parameters to an $R(R_w)$ value of 0.0472 (0.0525). The function minimized was [∑w(|F_o| − |F_c|)^2/∑wF_o^2]$^{1/2}$, w = 1/σ^2(F_o). Residual electron densities: +1.67/−1.60 eÅ^{-3}, located at Sm(1) and Sm(2). Refinement of the inverse model gave $R(R_w)$ values of 0.058 (0.062).

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[(Me₃Si)₂P]Sm[μ-P(SiMe₃)₂]₃Sm(thf)₃ (1). In the glovebox, KP(SiMe₃)₂ (157 mg, 0.72 mmol) dissolved in 5 mL of tetrahydrofuran was added to a solution of SmI₂(thf)₂ (200 mg, 0.36 mmol) in 7 mL of tetrahydrofuran to give a purple suspension. After 20 min, the reaction mixture was centrifuged. Removal of solvent and subsequent crystallization from toluene at −30 °C gave **1**·C₇H₈ as dark purple crystals (119 mg, 50%): ¹H NMR (C₆D₆, 270 MHz, 20 °C) δ 1.10 (s, $\nu_{1/2}$ = 20 Hz). ¹H NMR (C₇D₈, 270 MHz, 20 °C) δ 0.99 (s, $\nu_{1/2}$ = 20 Hz). ¹H NMR (C₇D₈, 270 MHz, −20 °C) δ 5.9 (vbr), 4.1 (vbr), 3.8 (vbr), 2.6 (vbr), 1.60 (s, $\nu_{1/2}$ = 10 Hz), −0.4 (vbr), −2.5 (vbr). ¹H NMR (C₇D₈, 270 MHz, −80 °C) δ 13.6 (vbr), 8.5 (vbr), 6.1 (vbr), 3.8 (vbr), 3.09 (s, $\nu_{1/2}$ = 10 Hz), −0.54 (br), −2.93 (br). ¹H NMR (C₄D₈O, 400 MHz, 20 °C) δ 0.42 (s, $\nu_{1/2}$ = 10 Hz). ¹H NMR (C₄D₈O, 400 MHz, 0 °C) δ 0.52 (s, $\nu_{1/2}$ = 117 Hz). ¹H NMR (C₄D₈O, 400 MHz, −20 °C) δ 0.85 (br, $\nu_{1/2}$ = 170 Hz), 0.28 (vbr). ¹H NMR (C₄D₈O, 400 MHz, −40 °C) δ 1.18 (s, $\nu_{1/2}$ = 67 Hz), 0.06 (s, $\nu_{1/2}$ = 84 Hz). ¹H NMR (C₄D₈O, 400 MHz, −60 °C) δ 1.60 (s, $\nu_{1/2}$ = 25 Hz), 0.03 (s, $\nu_{1/2}$ = 23 Hz). ¹H NMR (C₄D₈O, 400 MHz, −80 °C) δ 2.38 (s, $\nu_{1/2}$ = 18 Hz), 0.03 (s, $\nu_{1/2}$ = 11 Hz). ¹H NMR (C₄D₈O, 400 MHz, −100 °C) δ 3.94 (s, $\nu_{1/2}$ = 16 Hz), −0.01 (s, $\nu_{1/2}$ = 8 Hz). IR (Nujol) 1494 w, 1294 w, 1238 s, 1028 s, 823 vs, 728 s, 694 w, 676 m, 624 s, 520 w, 464 s, 425 m cm⁻¹. Anal. Calcd for C₄₃H₁₀₄O₃P₄Si₈Sm₂: C, 39.17; H, 7.95; P, 9.40. Found: C, 38.83; H, 7.80; P, 9.13. Magnetic susceptibility: X_M^{293K} = 4.33 × 10⁻³ cgs; μ_{eff} = 3.2 BM.

Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (11 pages). Ordering information is given on any current masthead page.

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